

Template Preparation of Nanoelectrode Ensembles -
Achieving the "Pure-Radial" Electrochemical-Response Limiting Case

John C. Hulteen, Vinod P. Menon, and Charles R. Martin*

Department of Chemistry
Colorado State University
Ft. Collins, Colorado 80523

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

19960624 248

*Corresponding author

DTIC QUALITY INSPECTED 1

Abstract

We have been investigating a new method for preparing ensembles of disk-shaped nanoscopic electrodes. This method entails deposition of the electrode material into the pores of a nanoporous membrane. Nanoscopic wires of the electrode material, with monodisperse diameters, are obtained in each pore. The ends of these nanowires (at one face of the membrane) define the ensemble of disk-shaped nanoelectrodes. We call this approach for preparing nanoelectrode ensembles (NEEs) the template method. In all of our prior investigations the electrode elements in the NEE were so close together that the diffusion layers at the elements overlapped. This is called the "total-overlap" electrochemical-response limiting case. In this paper we demonstrate (for the first time) that it is possible to use the template method to prepare NEEs with elements so widely spaced that the diffusion layers are completely isolated. The key to achieving this "pure-radial" limiting case is obtaining template membranes with very low porosities.

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-91J-0201

R&T CODE: 4133032

Robert J. Nowak

TECHNICAL REPORT NO. 48

by John C. Hulteen, Vinod P. Menon and Charles R. Martin

Prepared for Publication

in *J. Chem. Soc. Faraday Trans.*

Colorado State University
Department of Chemistry
Fort Collins, CO 80523-1872

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

REPORT DOCUMENTATION PAGE

2. June 13 , 1996
3. Interim report
4. "Template Preparation of Nanoelectrode Ensembles--Achieving the 'Pure-Radial' Electrochemical-Response Limiting Case "
5. GRANT: N00014-91J-0201 , R&T CODE: 4133032
6. John C. Hulteen, Vinod P. Menon and Charles R. Martin
7. Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872
8. TECHNICAL REPORT NO. 48
9. Office of Naval Research, Chemistry Division, 800 North Quincy Street, Arlington, VA 22217-5660
11. To be published in J. Chem. Soc. Faraday Trans.
12. Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.
13. Abstract: We have been investigating a new method for preparing ensembles of disk-shaped nanoscopic electrodes. This method entails deposition of the electrode material into the pores of a nanoporous membrane. Nanoscopic wires of the electrode material, with monodisperse diameters, are obtained in each pore. The ends of these nanowires (at one face of the membrane) define the ensemble of disk-shaped nanoelectrodes. We call this approach for preparing nanoelectrode ensembles (NEEs) the template method. In all of our prior investigations the electrode elements in the NEE were so close together that the diffusion layers at the elements overlapped. This is called the "total-overlap" electrochemical-response limiting case. In this paper we demonstrate (for the first time) that it is possible to use the template method to prepare NEEs with elements so widely spaced that the diffusion layers are completely isolated. The key to achieving this "pure-radial" limiting case is obtaining template membranes with very low porosities.
14. Subject terms: Nanoelectrodes, nanomaterials, electrochemistry
17. 18. 19. Unclassified

INTRODUCTION

We have developed a new method for preparing ensembles of disk-shaped ultramicroelectrodes.^{1, 2, 3, 4} This method entails deposition of the electrode material (e.g. Pt¹, carbon paste², Au³) into the pores of a microporous membrane to form microscopic wires of the electrode material. The membranes employed have cylindrical pores with monodisperse pore diameters.⁵ The microscopic wires formed in these pores are likewise monodisperse. The ends of these wires (at one face of the membrane) define the ensemble of disk-shaped ultramicroelectrodes. We call this the "template method"⁵ because the pores in the membrane act as templates for the electrode elements. This method can be used to prepare ensembles of disk-shaped electrodes with diameters as small as 10 nm.³

The membranes used in all of our previous work were commercially-available filters. Because these membranes are sold as filters, they must have as high a porosity as is technologically possible⁶. This has an interesting consequence for the electrochemical application of these membranes - all of the electrode ensembles that we have prepared to date have operated in the "total-overlap" electrochemical-response limiting case.^{1, 2, 3} This means that, because of the high porosity, the diffusion layer created at each individual electrode element overlaps with the diffusion layers created at its neighboring elements.

While this total-overlap limiting case is electrochemically important,³ another electrochemical-response limiting case - called the "pure-radial" case^{1, 2}

- is also important. This limiting case would be obtained from a membrane with such low porosity that the diffusion layer created at each electrode element is completely isolated from the diffusion layers created at its neighbors. Because such low porosity membranes are not commercially available, we have never been able to achieve this pure-radial case.

If it could be achieved, the pure-radial case would offer some interesting opportunities. For example, this case would yield classical sigmoidal voltammograms, and the total steady-state current (i_{ss}) at the ensemble would simply be the current at one of the elements ($i_{ss} = 4nFDCr$, where D is the diffusion coefficient, C is the concentration, and r is the radius of disk) multiplied by the number of elements in the ensemble.² Furthermore, this case would be very easy to simulate and model since the theory for a single ultramicrodisk electrode is well known.⁷ This would be particularly advantageous in investigations of electrode kinetics at such electrodes.^{3,7}

We have recently obtained membranes that are like those used in our previous studies but have much lower pore densities. Electrode ensembles have been prepared from these low pore density membranes, and we have found that the membrane with the lowest pore density (4×10^4 pores cm^{-2}) achieves the pure-radial limiting case. This was proven by matching experimental and simulated voltammograms, where the simulation assumes the pure-radial case. The results of these investigations are described here.

EXPERIMENTAL

Materials. Anhydrous SnCl_2 (Aldrich), AgNO_3 (Spectrum), trifluoroacetic acid, Na_2SO_3 , NH_4OH , formaldehyde solution (37%w/w), anhydrous methanol, concentrated HNO_3 , and NaNO_3 (Mallinckrodt) were used as received. Purified water was obtained by passing house distilled water through a Milli-Q (Millipore) water purification system. Oromerse SO Part B, a commercial gold plating solution (Technic Inc.), was diluted 40 times with water prior to use. [(Trimethylamino)methyl]ferrocene (TMAFc^+) perchlorate was prepared according to the literature reference.⁸

"Track-etch" ⁶ polycarbonate and polyester membrane filters were obtained from Poretics and Cyclopore. The characteristics of these membranes are shown in Table I. Note that both polyester and polycarbonate membranes were obtained. All of our prior work has been done with polycarbonate membranes. The pore densities and diameters were provided by the suppliers, but we have used scanning electron microscopy (SEM)³ to verify these numbers. The average center-to-center distance between pores was calculated according to reference 9. This is called the "average" distance because the pores are randomly distributed across the face of the membrane.

Measurements. All voltammetric measurements were performed using a PAR Model 273-potentiostat in conjunction with a PAR Model 175 programmer and a Soltec Model VP6424S X-Y recorder or a Nicolet Model 310 digital storage oscilloscope. Digital simulations were carried out using DIGISIM (BAS Inc.), a cyclic voltammetric simulations program, running on an ACT Model 486/66-520 E/S computer. SEM images were obtained on a Philips 505 microscope.

Electrode Fabrication. Electroless plating methods were used to deposit gold nanowires into the pores of these membranes. One of the methods used here was described in detail in ref. 3. This method was developed specifically for electroless plating of Au into the pores of the polycarbonate membranes. A variant of this method was developed for plating Au into the pores of the polyester membranes (Table I). Briefly, both methods entail applying a sensitizer (Sn^{2+}) to all of the surfaces of the membrane (i.e. the pore walls and both membrane faces). The sensitizer is then used to reduce Ag^+ to form nanoscopic Ag^0 particles on the membrane surfaces. These Ag^0 particles are then used to reduce Au(I) to form analogous Au^0 particles on the membrane surfaces. The Au^0 particles are excellent auto catalysts for the electroless reduction of Au(I) to Au^0 , using formaldehyde as the reducing agent.³

The electroless plating procedure used to deposit Au in the pores of the polycarbonate membranes (Table I) is identical to that described in ref. 3. This procedure had to be modified in order to accomplish Au deposition into the pores of the new polyester membranes (Table I). The modifications are as follows: 1. A lower concentration of SnCl_2 (0.0026 M vs. 0.026 M) was used to sensitize the polyester membrane. This was necessary because the polyester membrane has more Sn^{2+} binding sites on its surfaces than does the polycarbonate membrane used previously.³ 2. The Au plating bath and plating procedure were essentially identical to those used previously³ except that the reducing agent (formaldehyde solution) was added in two 0.6 mL portions (to a total bath volume of 20 mL). The first aliquot was added at the beginning of Au

plating and the second was added half way through the plating process. The total plating time was 24 hrs.

Electrodes were prepared from the Au-plated membranes using the procedure described previously.³ The geometric area of the membrane exposed to the solution in these electrodes is 0.079 cm². For comparison, a conventional Au disk electrode with an area of 0.079 cm² was also prepared.³ We call such conventional electrodes "macro" electrodes.

RESULTS AND DISCUSSION

Membranes. The microporous membranes used here are described in Table I. Note, first, that the pores in these membranes are very small, and as a result, the disk-shaped electrode elements obtained are correspondingly small. We call ensembles containing such truly nanoscopic electrode elements nanoelectrode ensembles or NEEs.³ Memb1 in Table I is the commercially-available 100 nm pore-diameter filter. The other membranes were obtained by special order from the manufacturers. Note that the key difference is the lower pore densities. It is these lower pore densities that allow us to achieve the pure-radial electrochemical-response limiting case.

Scanning Electron Microscopy. SEM images of the surfaces of the four membranes used here, after deposition of the Au nanoelectrode elements, are shown in Figure 1. The disk-shaped electrode elements appear as bright spots against a black background (the membrane surface). The streaks that are often seen in these images occur because secondary electrons can penetrate a finite distance through the polymeric membrane. As a result some electrons that

originated from the Au nanowire, imbedded in the pore are detected. All images in Figure 1 were taken at the same magnification in order to emphasize the difference in spacing between the electrode elements.

The SEM image in Figure 1A shows that, at this magnification, it is difficult to distinguish the individual electrode elements in the high pore density polycarbonate membrane (Memb1). This becomes easier in the images of the two intermediate pore-density membranes (Memb2, Figure 1B; Memb3, Figure 1C). The pore density in Memb4 is so low that, in principle, only one electrode element would be seen in the image in Figure 1D. More are seen because of the random nature of the spacing between the pores/elements.

Double-layer charging currents. A persistent problem with micro and nanoelectrodes is the sealing of the conductive electrode element to the insulating material that surrounds the element such that solution does not creep into this junction.^{1,3,10} We have shown that with the polycarbonate template membranes, this problem can be solved by heating the polycarbonate above its glass transition temperature.³ This results in relaxation of the polymer around the Au nanowires in the pores, and this seals the polymer to the nanowire surface. Figure 2 shows that this method also works with the polyester membranes.

Curve A in Figure 2 shows double layer charging currents for an Au macro electrode with an area equivalent to the exposed membrane area of the NEEs (0.079 cm²). Curve B in Figure 2 shows analogous double layer charging currents for a NEE prepared from the polyester membrane, Memb2, before

thermal processing to seal the Au nanowires. If only the disk-shaped ends of the Au nanowires are exposed to the solution, a double layer charging current of ca. 1 nA would be predicted, based on the known double layer capacitance of Au³ and the known fractional pore area of the NEE (Table I). The much larger current in Figure 2B clearly shows that electrolyte is creeping between the pore wall and the Au nanowire³. After thermal processing (Curve C) the double layer charging currents have dropped to very close to the predicted value, indicating that Au nanowires have now been effectively sealed.

Faradaic Currents. Figure 3 shows cyclic voltammograms (50 mV s⁻¹) for TMAFc⁺ at NEEs prepared from the four membranes in Table I. Memb1 has one of the highest fractional pore areas we have investigated to date. As a result, we would expect NEEs prepared from this membrane to be in the total-overlap limiting case at the low scan rate used in Figure 3. The peak-shape voltammogram, with 60 mV peak separation (Figure 3, Curve A), clearly suggests that this is the case.

We can quantitatively prove that this is the case by comparing experimental and simulated voltammograms. Such a comparison is shown in Figure 4A. The simulated voltammogram is based on the reversible total-overlap limiting case,³ and other than assuming an arbitrarily-large value of the standard heterogeneous rate constant, there are no adjustable parameters. The quantitative agreement between the simulated and experimental voltammograms proves that NEEs prepared from Memb1 are in the total-overlap electrochemical case at a scan rate of 50 mV s⁻¹.

At the other extreme, Memb4 has, by far, the lowest fractional pore area of any membrane to be investigated to date. The large average distance between pores (Table I) suggests that NEEs based on this membrane will be in the pure-radial limiting case at nearly any experimentally-accessible scan rate. The classic sigmoidal voltammogram shown in Figure 3 curve D suggests that this is, indeed, the case. Again, we can quantitatively prove this by comparing experimental and simulated voltammograms. Figure 4B shows this comparison. The simulation assumes a single 200 nm-diameter disk electrode, with currents multiplied by the number of such electrodes in the NEE. The quantitative agreement between the simulated and experimental voltammograms proves that we have, for the first time, achieved the pure-radial limiting case with a template-based NEE.

Memb2 and Memb3 have fractional pore areas intermediate between the two extremes discussed above. We would expect, therefore, electrochemistry that is somewhere between the total-overlap and pure-radial limiting cases.¹¹ Furthermore, we would expect that NEEs made from Memb2 would more closely approximate total-overlap behavior, while NEEs made from Memb3 would more closely approximate the pure-radial case. Curves C and D in Figure 3 show that these expectations are qualitatively achieved.

It is much more difficult to simulate these intermediate voltammetric cases. Indeed, to our knowledge, code that allows for simulation of cyclic voltammograms at a random ensemble of nanoelectrodes has never been written. Furthermore, from a practical point of view (e.g. from the point of view of

using these NEEs for electrode kinetic studies³ these intermediate cases are much less interesting than either the pure-radial or total-overlap cases.

CONCLUSIONS

We have demonstrated, for the first time, that NEEs prepared via the template method can quantitatively achieve the pure-radial limiting case. We believe that the ease with which this case can be simulated, for both reversible and quasi-reversible electrochemistry, will make these new NEEs particularly useful for investigations of heterogeneous kinetics of fast redox couples.^{3,7} We are currently using these NEEs for this purpose. Finally, these NEEs have the added advantage, over a single nanoelectrode, of producing easily-measurable currents, because the net current at the NEE is the current that would be obtained at a single nanoelectrode multiplied by the number of electrode elements in the NEE.

Acknowledgments. This work was supported by the Office of Naval Research.

References

- (1) R. M. Penner and C. R. Martin, *Anal. Chem.*, 1989, **59**, 2625.
- (2) I. F. Cheng, L. D. Whiteley and C. R. Martin, *Anal. Chem.*, 1989, **61**, 762.
- (3) V. P. Menon and C. R. Martin, *Anal. Chem.*, 1995, **67**, 1920.
- (4) M. Nishizawa, V. P. Menon and C. R. Martin, *Science*, 1995, **268**, 700.
- (5) C. R. Martin, *Science*, 1994, **266**, 1961.
- (6) R. L. Fleischer, P. B. Price and R. M. Walker, *Nuclear Tracks in Solids, Principles and Applications*, University of California Press, Berkeley, CA, 1975.
- (7) A. M. Bond, K. B. Oldham and C. G. Zoski, *Anal. Chim. Acta*, 1989, **216**, 177.
- (8) M. N. Szentirmay and C. R. Martin, *Anal. Chem.*, 1984, **56**, 1898.
- (9) B. R. Sharifker, *J. Electroanal. Chem.*, 1988, **240**, 61.
- (10) K. R. Wehmeyer and K. R. Wightman, *J. Electroanal. Chem.*, 1985, **196**, 417.
- (11) C. Amatore, J. M. Saveant and D. Tessier, *J. Electroanal. Chem.*, 1983, **147**, 39.

Figure Captions

Figure 1. SEM images of the surfaces of NEEs prepared from the membranes in Table I. A. (top left) Memb1. B. (top right) Memb2. C. (bottom left) Memb3. D. (bottom right) Memb4. In all micrographs, the sample was sputtered with a thin film (< 30 nm) of a Pd/Au alloy prior to imaging in order to eliminate surface charging.

Figure 2. Cyclic voltammograms in 50 mM NaNO_3 (100 mV s^{-1}). A. Au macroelectrode. B. NEE prepared from Memb2 (Table I) before thermal processing. C. As per B, but after thermal processing.

Figure 3. Cyclic voltammograms (50 mV s^{-1}) for 50 mM TMAFc^+ in 5 mM NaNO_3 for NEEs prepared from the membranes in Table I. A. Memb1. B. Memb2. C. Memb3. D. Memb4.

Figure 4. Simulated (00000) and experimental (----) voltammograms for NEEs prepared from A. Memb1. B. Memb4. Scan rate and solution as per Figure 3. See text for details of the simulations.

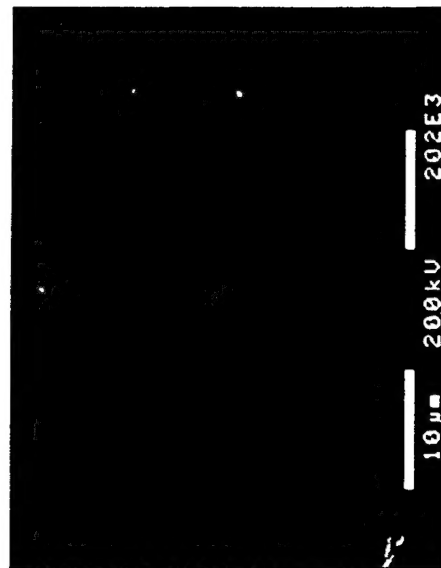
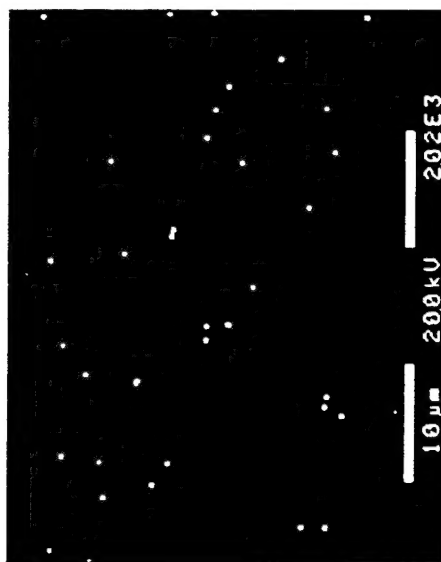
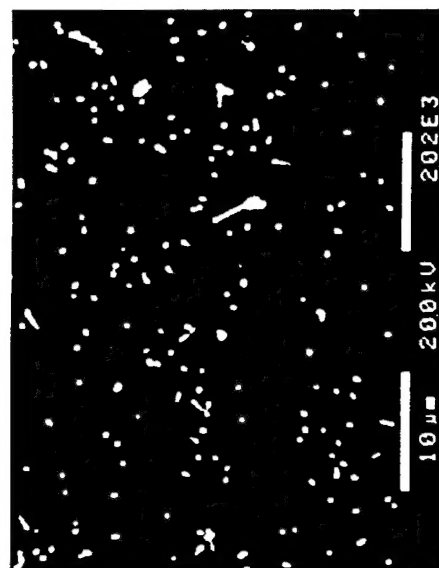
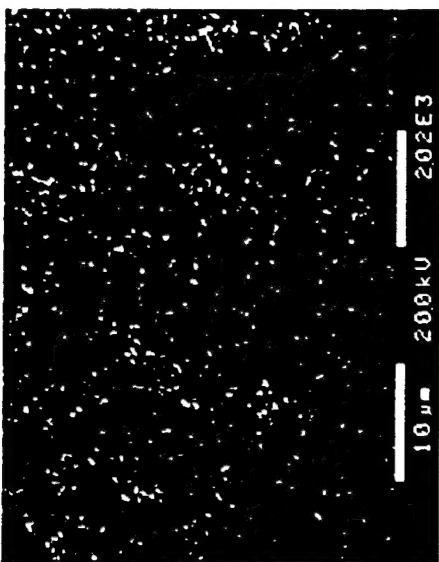
Table 1. Membrane characteristics

Membrane Designation	Pore Diameter (nm)	Distance between pores (μm)	Fractional pore area ^a	Material
Memb1	100	0.25	3.1×10^{-2}	PC ^b
Memb2	200	1.1	6.3×10^{-3}	PE ^c
Memb3	200	3.5	6.3×10^{-4}	PE
Memb4	200	25	1.3×10^{-5}	PC

^a Active electrode area determined by nominal pore density and diameter divided by the total geometric area.

^b PC = polycarbonate

^c PE = polyester



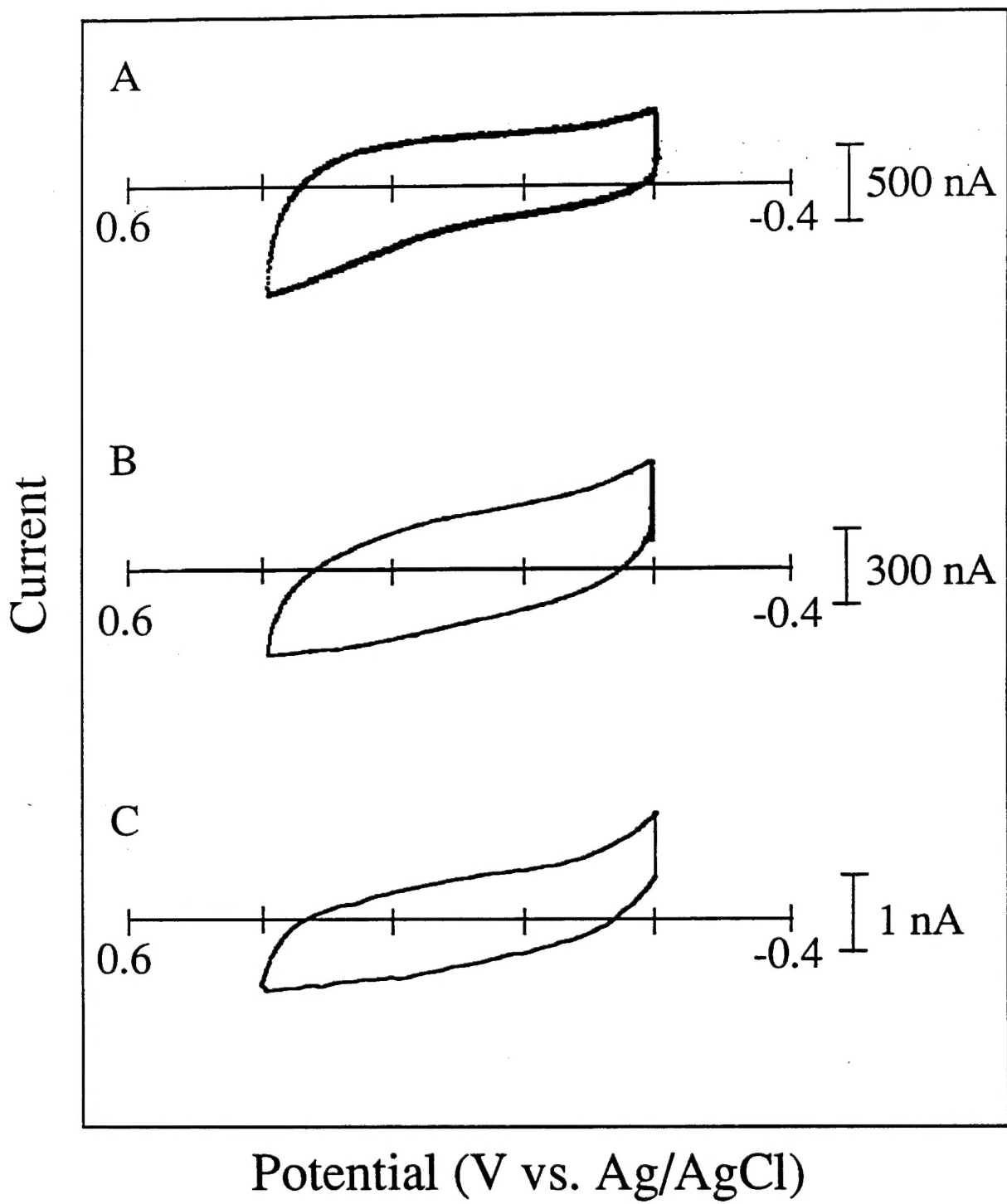


Figure 2

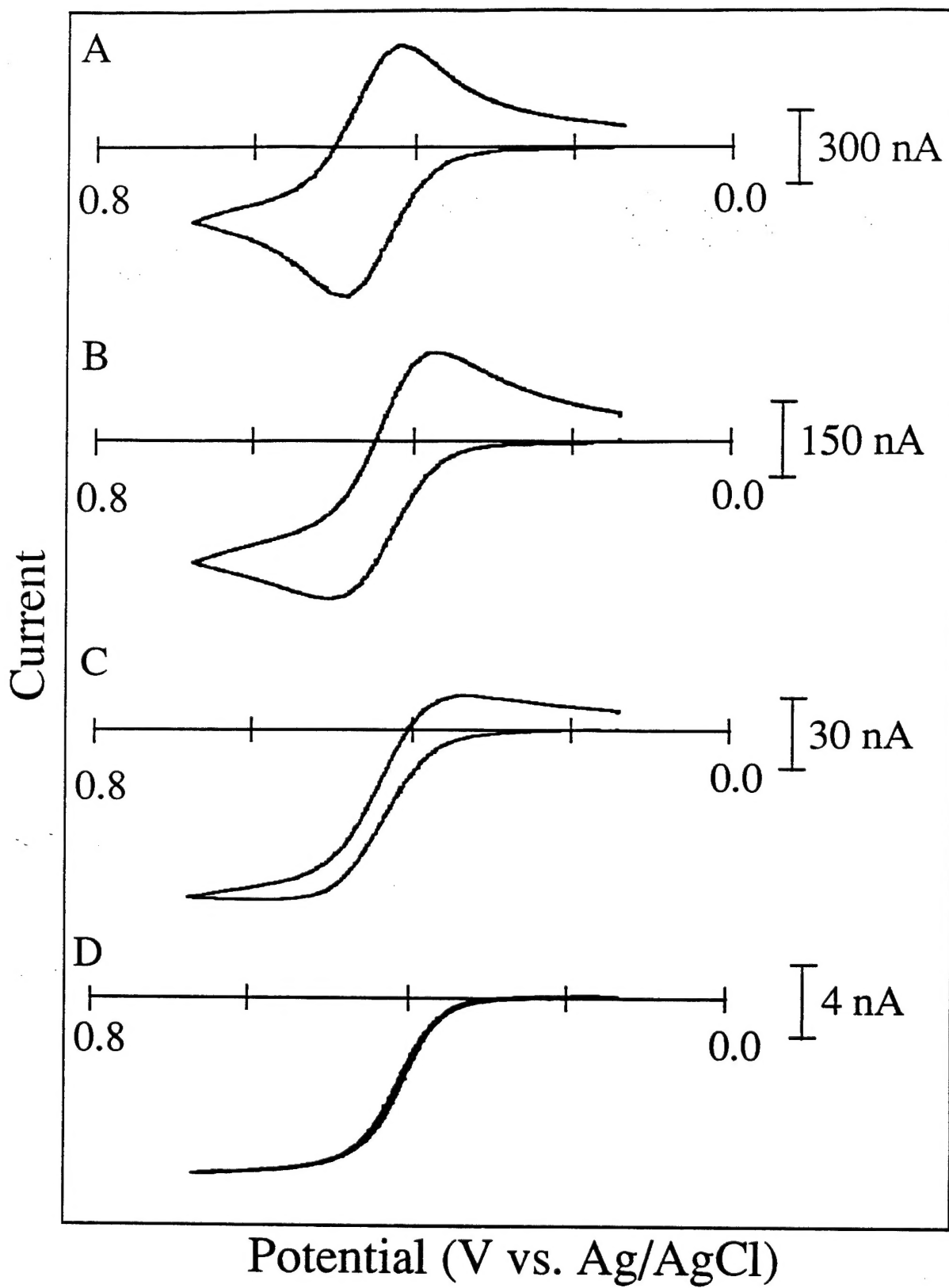


Figure 3

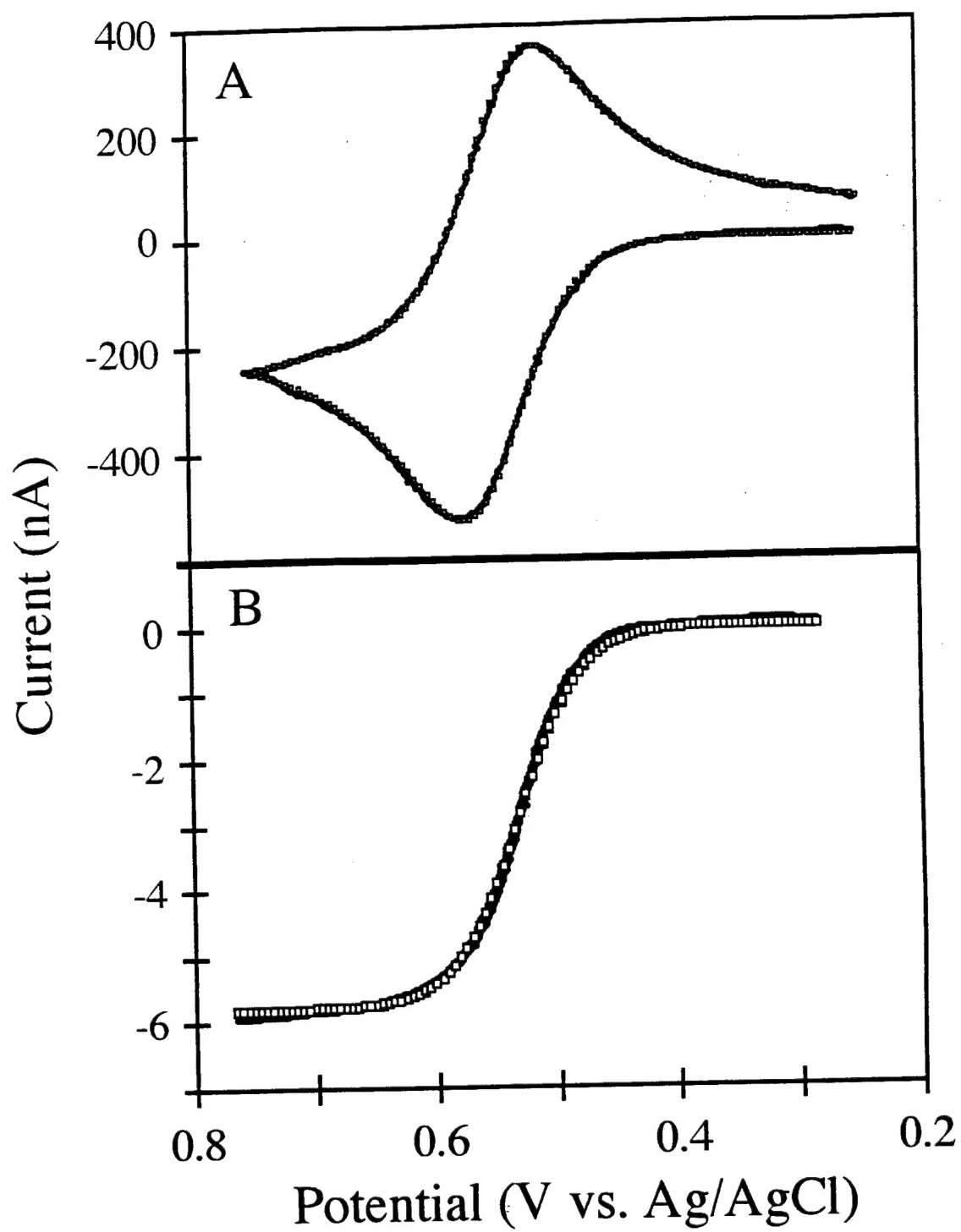


Figure 4